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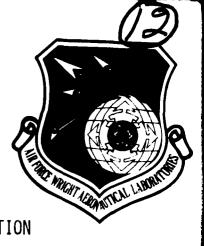
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ADVANCED CARBON FABRIC/PHENOLICS FOR THERMAL PROTECTION APPLICATIONS

D. L. SCHMIDT

R. D. CRAIG

COATINGS AND THERMAL PROTECTIVE MATERIALS BRANCH NONMETALLIC MATERIALS DIVISION

FEBRUARY 1982

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FINAL REPORT FOR PERIOD 1 SEPTEMBER 1980 - 1 AUGUST 1981

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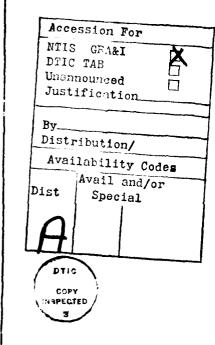
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| because of their low conductivity, dimensional | stability and strength at very |
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| over two decades, these carbonaceous fibers have | e been manufactured from pre- |
| | ion has been focused on the |
| precursor polyacrylonitrile because of its high | |
| availability in various filament count yarns and | |
| to high-strength carbon fibers. An assessment v | was therefore (cont a) |

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conducted to identify the attributes of PAN-based carbon fabrics for thermal protection composites. Commercially available PAN-based carbon fabrics exhibited high strength and uniformity, but they were deficient in insulative and chemical purity characteristics. To alleviate these limitations, a variety of high-purity PAN-based carbon fabrics were manufactured at maximum processing temperatures from 900° to 1,350°C. These specialty fabrics were prepregged with phenolic resin and fabricated into flat laminates and tapewrapped cylinders. Engineering properties were measured and correlated with the precursor fabric characteristics. PAN-based carbon fabric manufactured at a maximum processing temperature of 1,075°C appeared to have the best balance of insulative, ablative and mechanical properties. Further reduction in alkali metal contaminants and improved fiber-to-matrix bonding are needed to enhance their potential use in heatshielding applications.



FOREWORD

This report describes an in-house effort conducted by personnel of the Coatings and Thermal Protective Materials Branch, Nonmetallic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. The effort was conducted under Project 2417, "Thermal Protection Materials," Task 241701, "Strategic Missile Protective Materials."

The work reported herein was performed during the period 1 September 1980 and 1 August 1981, under the direction of the authors, Mr Donald L. Schmidt and Dr Robert D. Craig (AFWAL/MLBE), Project Engineers. The report was released by the authors on 1 August 1981.

Some of the items described in this report were commercial items that were not developed or manufactured to meet any Government specifications, to withstand the tests to which they were subjected, or to function as applied during this study. Any failure to meet the objectives of this study is no reflection upon any of the commercial items discussed herein or upon any manufacturer.

The authors gratefully acknowledges the contributions of Mr Paul Roy,
Avco Corporation; the Celanese Corporation for preparation of the developmental carbon tows; Textile Products, Incorporated for weaving the specialty carbon tows; U.S. Polymeric, Incorporated for preparation of phenolic prepregs;
Hitco Corporation for fabrication of plastic composites; the Southern Research Institute for measurement of physical, thermophysical and mechanical
properties of composites and the Avco Corporation for measurement of the
ablative and insulative characteristics.

The authors acknowledge with appreciation the use of the following illustrations: Figure 3, DOE Sandia Laboratories; Figure 5, PDA, Engineering; Figure 6, PDA, Engineering; Figure 7, Avco Corporation Systems Division; and Figure 8, Acurex Corporation.

A major portion of this report was presented at the 26th National SAMPE Symposium and Exhibition, Los Angeles, California, 28-30 April 1981. The presentation was titled "PAN-Based Carbon Fabrics for Thermal Protection Composites," and published in <u>Material and Process Applications, Land</u>, Sea, Air, Space, Vol. 26, SAMPE, Azusa, CA, pp. 504-515.

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SECTION I

INTRODUCTION **

Carbon fibers possess extraordinary structural, weight, and thermal properties, which lend themselves to many new uses in commercial and defense applications. Some of the important commercial uses include: sporting goods, automobile structures, aircraft structures, spacecraft structures, propulsion systems, marine, self-lubricating bearings and gears, industrial, electrical, textile and packaging machinery, energy, gas centrifuges, medical and planetary entry probe protection (References 1 to 17). Several key defense applications are: military aircraft structures, aircraft brake systems, reentry vehicle thermal protection, missile structures, pressure vessels, helicopter components, antennas and radar screens, rocket nozzles, thrust chambers, turbine engines and armour (References 18 to 41).

Carbon fibers are used to reinforce composites when thermal stability, dimensional stability, strength, stiffness and weight are important considerations. Yarns or tows containing 400 to 160,000 individual filaments are commercially available in various forms, including unidirectional impregnated tapes up to 48 inches in width, multiple layers of tape with individual layers at selected fiber orientations, and woven fabrics of many weights and constructions.

Carbon fibers are widely used in thermal protection composites because of their low thermal conductivity, dimensional stability at high temperatures, low density, nonflammability, low cost and availability in a variety of physical forms. These fibers are typically woven into various fabric constructions and then combined with a char-forming resin to obtain the desired composite.

^{*}Technical terminology is defined in Appendix A.

The first continuous carbon fibers were manufactured industrially by the pyrolysis of regenerated cellulose (rayon) in an inert atmosphere.

Over 200 types of rayon yarn were evaluated to obtain the best balance of rayon-to-carbon yield, fiber strength and handling qualities. The original fibers, however, were of poor quality, low strength and low modulus. As properties increased, rayon continued to be the preferred precursor because of its ease in converting to a carbonized product, domestic availability, low cost, and availability from several sources (References 42-52). In recent years, there has been a sharp decline in using rayon fiber precursors because of the loss of suitable domestic sources and the demonstrated performance of alternate precursor carbon fibers. For example, only one domestic source presently exists for the manufacture of suitable rayon filaments. The continued availability of continuous filament rayon is thus questionable because only a small volume is required for defense needs and these requirements are highly cyclic (Reference 53).

Polyacrylonitrile (PAN) fibers are a promising replacement for rayon in the manufacture of carbon fibers. A wide range of fiber properties are available, as demonstrated by almost two decades of research conducted in Japan and England (References 54 to 56). Another alternate precursor fiber is based on petroleum pitch because of its low-cost potential, domestic availability and attractive fiber stiffness in carbonized form. The fiber technology is not as well developed, however, as compared to PAN-based materials.

The objective of this materials program was to determine the suitability of commercial and developmental PAN-based carbon fibers for missile heatshielding uses.

SECTION II

PRECURSOR FIBER GOALS

Fibrous precursors used in the manufacture of carbon fibers should be homogeneous, strong, relatively inexpensive, and commercially available. The virgin fiber should possess a high carbon content and retain a maximum of the carbon content in the pyrolyzed residue. They should have a melting temperature substantially higher than its decomposition temperature. Contaminates should be a minimum in the virgin and pyrolyzed fibers. Pyrolysis should proceed in an orderly fashion and without large exotherms. Energy requirements should be minimum (References 57 and 58).

SECTION III

PRECURSOR PAN FIBERS

PAN fibers are produced from high molecular weight, linear organic compounds. They are either homopolymers, copolymers, terpolymers, or graft polymers. Copolymeric fibers have been found to be the most suitable for producing fibrous carbons. Their chemical compositions vary somewhat, but in all cases, they contain not less than 85 mol % acrylonitrile and not more than 15 mol % (usually three to six percent) of a monovinyl compound such as methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidine chloride, or the like. A representative PAN fiber chemical composition is 68 weight % carbon, 26 weight % nitrogen, and 6 weight % hydrogen.

Continuous and staple PAN fibers are spun by either a wet or dry process. In the wet process, the polymer is batch produced, blended, and dissolved in a hot solvent like dimethyl formamide (DMF) or sodium thiocyanate. A polymer solution of about 15 weight % is degassed, filtered and then extruded under pressure through spinnerettes (multiple-holed jets) having from 1,000 to 12,000 holes and a diameter from two to 20 thousandths of an inch. The spinnerettes are immersed in a coagulation bath, which is typically 85% DMF and 15% water. Fiber formulation commences at the face of the spinnerettes by the action of the non-solvent in the bath. The newly formed fiber is essentially a swollen gel consisting of a mixture of polymer, solvent and non-solvent. The fiber structure and properties are sensitive to the coagulation bath temperature, and, the mechanical properties are determined by the percent of drawing (stretching) of the fiber. In the dry-spinning process, the PAN fiber is extruded through the spinnerette virtually downwards into an ascending column of heated air, nitrogen or steam where the

solvent is vaporized and solidified filaments are formed. Various processes may be subsequently performed, including washing, hot stretching (about 100° C), drying, crimping, and cutting (Reference 59).

Control of the Contro

Staple fiber is prepared by cutting or breaking very large continuous filament tow to prescribed lengths (0.5 to 4.0 inches). Fiber spinning is essentially the same for both types, but significant economical advantages are achieved with staple materials. Large, multiple-hole (25,000 to 40,000) spinnerettes are used, compared to the typical 720 to 6,000 filament spinnerattes used to make small diameter yarns for the aerospace industry. Some limitations of staple fibers are lower strength yarn and fabric, greater thickness yarn and fabric, and additional manufacturing steps to card the fibers and ply into yarns. Initial attempts to use staple fiber carbon fabrics in thermal protective composites have been disappointing because of their unpredictable and somewhat erratic ablation behavior in very high temperature gases.

PAN fibers are available in the U.S. from about three domestic sources and ten foreign sources. Fibers in carbonaceous products are largely imported from Great Britain and Japan. Tow, staple yarn, and continuous yarns are used but for economic reasons, large-diameter tows such as 10,000 to 160,000 filaments are most common.

PAN fibers are suitable precursors for carbonaceous materials. They have a high carbon content, low costs, available in numerous filament count yarns and tows, stable commercial market, and multiple producers. Special grades of PAN fibers are usually used, however, to obtain superior carbon properties and faster processing times. Such specialty fibers are much more expensive than the high-volume, commercial PAN fibers.

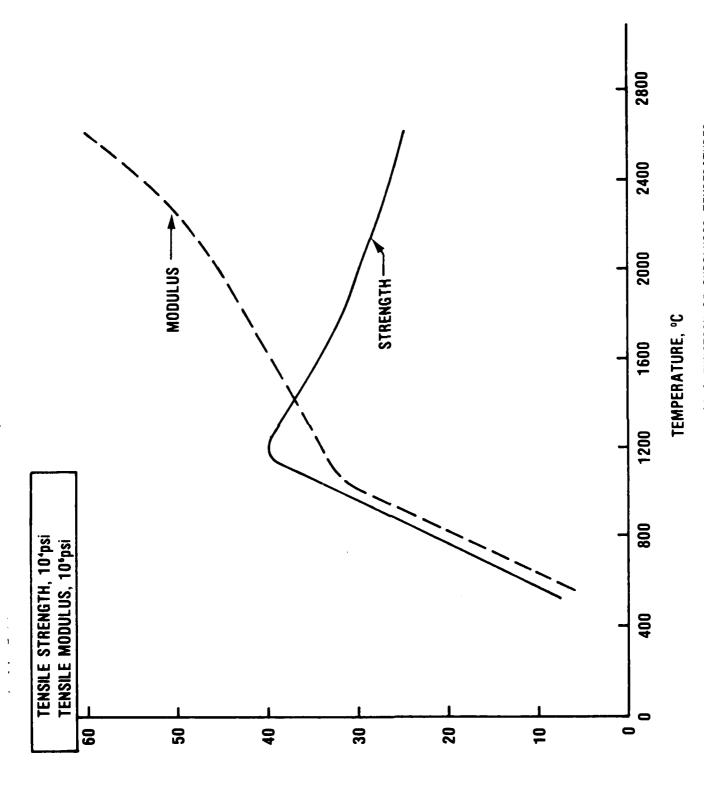
Defense applications for carbon fibers may invoke three additional requirements, namely, ultra-high performance, small diameter yarns and tows and very pure fibers. Very high strength and modulus carbon fibers have been demonstrated by the removal of particulate matter. Surface flaws were significantly reduced, which in turn, produced dramatic increases in tensile strength. Thin fabrics for ablative applications require a small number of filaments per yarn or tow for weaving into fabrics. Finally, alkali metal contents of several hundreds to thousands parts per million for commercial fibers have to be significantly reduced to minimize the electron concentration in the ablation products-air flow surrounding and trailing hypersonic reentry vehicles.

SECTION IV

CARBON FIBER FORMATION

Carbon fibers have been derived from PAN precursors since the early 1960's (Reference 54). Most of the research to date has been devoted to obtaining the highest possible tensile strength, strain-to-failure, and an acceptable tensile modulus. As shown in Figure 1, carbonization of PAN fibers at about 1,250°C to 1,350°C and in an inert atmosphere produces a high-tensile-strength product of intermediate modulus. With increase in the maximum pyrolysis temperature, the fiber tensile strength first increases and then decreases (due to increased defects) whereas the tensile modulus continues to increase monotonically with temperature (due to increased ordering of the carbon atoms). PAN-based carbon fibers intended for strength-limiting applications are slowly processed at 1,000°C to 1,600°C (preferably 1,200°C to 1,350°C). PAN-based graphite fibers destined for stiffness-limiting applications are manufactured at significantly higher temperatures (over 2,400°C), but their costs are significantly higher.

Carbon fiber formation processes are complex, but believed to be as follows. The nitrile groups are partially polymerized either by self-initiation or by the action of foreign side groups, e.g., comonomers. Dehydration of the polymer occurs at the same time. During this process, the fiber length is held constant and shrinkage is prevented. Pretreatment of the fibers with a Lewis acid accelerates these processes. The linear structure is transformed into a stable ladder structure, no longer fusible. On the contrary, cellulose fibers are disoriented during the first carbonization state and thus must be stretched during carbonization in order to achieve high strength and high modulus.



TENSILE PROPERTIES OF CARBON FIBERS AS A FUNCTION OF PYROLYSIS TEMPERATURES FIGURE 1.

The structure and properties of carbon fibers are controlled by the choice of raw material, heat treating cycle, use of chemical treatments during carbonization, and application of stress on the fibers during processing (References 60 to 71). Figure 2 illustrates the manufacturing process for PAN-based fibrous carbons, which is essentially a two-step process. PAN fibers are heated at 200° to 280°C for several hours in air to convert the thermoplastic structure into a ladder polymer (carbon atoms are arranged in hexagonal rings). The thermoset fibers thus do not melt upon subsequent heat treatment. Tension is used to restrain the fibers (prevent a 25 percent shrinkage) during the oxidation treatment and maximize structural properties. The stabilized fibers are then pyrolyzed (about 30 weight % is volatilized) in an inert atmosphere to increase the carbon content and minimize the residual hydrogen, oxygen and nitrogen contents. During the carbonization step, the cyclic molecular chains link up to form the more familiar layers of graphite structure.

Carbon fibers were initially manufactured by a batch process. Subsequent efforts have led to continuous, totally integrated manufacturing capabilities with significant price reductions and improved product quality. Today, a wide range of fibrous carbon products are, or soon will be, produced domestically including 1,000, 3,000, 6,000, 15,000 and 30,000 filament materials.

Carbon fibers derived from PAN retain their general morphology although they shrink biaxially during pyrolysis. Carbon fibers manufactured from wet spun PAN have characteristic round cross-sections and striated surfaces, as shown in Figure 3. Carbon fibers derived from dry-spun PAN are dog-boned in cross-section (References 70 and 71).

PAN-based carbon fibers have a higher carbon-fiber yield (60% vs 25%), can be processed into carbonized form in a shorter period of time, exhibit

PAN FIBER PRODUCTION

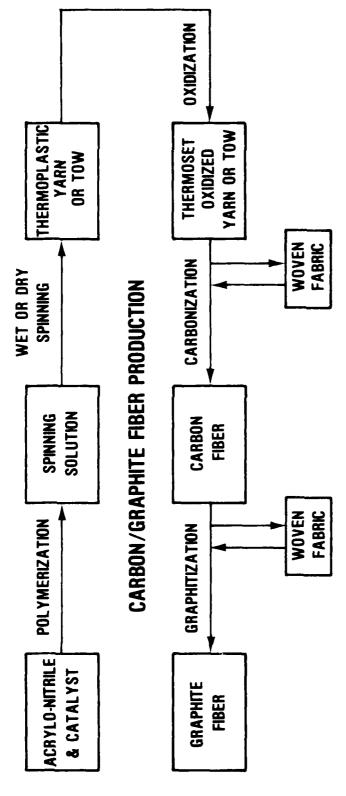


FIGURE 2. MANUFACTURE OF PAN-BASED FIBROUS CARBON PRODUCTS





CROSS-SECTIONS OF CARBON FIBERS DERIVED FROM WET-SPUN (LEFT) AND DRY-SPUN (RIGHT) PAN FIGURE 3.

a better balance of properties for a wide variety of composite applications, and are usually less expensive compared to rayon-based materials.

Representative properties of carbon fibers derived from PAN and two other chemically different precursors are given in Table 1. It is noted that carbonization temperatures on the order of 1,300° to 1,500°C produced very high strength (450 Kpsi), intermediate modulus (33 Mpsi), intermediate density (1.75 gm/cc) and high-carbon-content (92%) fibers. Typical properties of a commercially available PAN-based carbon yarn are shown in Table 2. Properties of a low modulus, rayon-based yarn are also given for comparative purposes.

TABLE 1

TYPICAL PROPERTIES OF CARBON YARNS

| | ٥ | ١ | , | | , |
|---|---|---|---|---|---|
| 1 | Ē | | | 5 |) |
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| | C | 1 | C | | |
| (| | 1 | Ì | _ | • |

| TYPE | POLYACRYLO. NITRII F (PAN) | RAYON |
|------------------------------|-------------------------------|------------|
| SOURCE | FOREIGN | DOMESTIC |
| SHAPE | ROUND | CRENULATED |
| LENGTH | CONTINUOUS | CONTINUOUS |
| PROCESS TEMP. °C, APPROX. | 1400-1500 | 1100-1200 |
| PROPERTIES | | |
| DIAMETER, MICRONS | ∞ | 7 |
| DENSITY, gm/cc | 1.75 | 1.53 |
| TENSILE STRENGTH, Kpsi | 450 | 120 |
| TENSILE MODULUS, Mpsi | 33 | 0.9 |
| ULTIMATE STRAIN, % | 1.3 | 2.0 |
| CARBON CONTENT, % | 92.0 | 90.0 |
| SURFACE AREA, sqm/gm | - | 130 |

TABLE 2

PROPERTIES OF PAN-BASED COMMERCIAL AND DEVELOPMENTAL CARBON FIBERS AND TOWS

| TOW DESIGNATION | HTA-7 | 06-125 | 06-112 | DG-114 | 06-110 | DG-129 900 |
|---|----------|------------|----------|--------|----------|---------------|
| FIBER PROPERTIES | 255.1 | , 150 | 20. | 5 | | |
| DENSITY, gm/cc | 1.76 | 1.74 | 1.80 | 1.80 | 1.78 | 1.76 |
| TENSILE STRENGTH, Kpsi | 400 | 375 | 348 | 291 | 278 | 220 |
| TENSILE MODULUS, Mpsi | 34.0 | 28.9 | 25.8 | 22.9 | 19.8 | 17.0 |
| CARBON CONTENT, % | 96 | 91 | 87 | 84 | 8 | 80 |
| ASH CONTENT, Wt. % | 0.21 | i | 0.16 | ł | 0.088 | 1 |
| TRACE METALS, ppm | 499 | 366 | 352 | 340 | ì | 294 |
| THERMAL STABILITY, % | | | | | | |
| LOSS thr IN 500°C AIR | 4 | 41 | 37 | 55 | 9 | 11 |
| MOISTURE CONTENT, % | 0.10 | ł | 5.7 | ļ | 6.9 | ł |
| TOW PROPERTIES | | | | | | |
| DENIER, gm/9,000m | 1,824 | 1,873 | 2,080 | 2,180 | 2,260 | 2,280 |
| ELECTRICAL RESISTIVITY, | | | | | | |
| micro ohm-cm | 1,500 | 3,228 | 6,610 | 19,153 | 57,214 1 | 114,400 |
| THERMAL CONTUCTIVITY, | | | | | | |
| cal/cm sec-°C (Est) | 0.032 | 0.010 | 0.00 | 0.007 | 0.006 | 90000 |
| *3,000 CONTINUOUS FILAMENT TOWS, CELANESE CORP. | IENT TOW | S, CEL ANE | SE CORP. | | | |

SECTION V

DEVELOPMENTAL CARBON TOWS AND YARNS

Commercially available carbon fibers derived from PAN precursors have been optimized for structural composites and sporting goods. Their highstrength and high-modulus characteristics are not needed in thermal protective composites, because the structural load is usually carried by a metallic substructure. Some sacrifice in fiber strength and modulus could thus be tolerated to achieve improved insulative, ablative and high-purity fiber properties.

A systematic investigation was conducted on the relationship between carbon fiber properties and the maximum pyrolysis temperature used in their manufacture. As shown in Table 2, a typical processing temperature of 1,350°C yielded carbon fibers with the highest: carbon content, strength, modulus, ash content and trace metals. Lower processing temperatures (900° to 1,125°C produced carbon fibers with substantially lower thermal conductivity (References 72 and 73). These specialty tows had desirable tensile strengths in excess of 220,000 psi, which is about double the value for rayon-based carbon fibers.

Note, however, that the low-temperature-fired tows had a low carbon content (about 80%) and a high nitrogen content (17%). A standard, commercially available carbon tow and four developmental grades of carbon tow were selected for further investigation.

SECTION VI

WOVEN FABRICS

PAN-based carbon fabrics are manufactured by two different processes, (References 74 to 76). Thermoset PAN yarns are woven into the desired fabric construction and then pyrolyzed, or the fabric is woven directly from carbon yarn or tow. Most PAN-based carbon fabrics manufactured today are obtained by weaving yarn or tow. This method permits a wide range of woven products, excellent structural properties and good handleability. The advantages and limitations of the methods for obtaining either processed or woven fabrics are given in Table 3. Fabric properties for woven oxidized PAN, carbonized woven oxidized PAN and woven carbon yarn are reported in Table 4.

Carbon fabrics were also woven from four developmental grades and one commercially available grade of carbon tow. The carbonized tows were obtained on a cardboard spool as a continuous six-inch-wide collimated band having multiple, 3,000 filament ends. This intermediate product was separated into 3,000 filament tows and re-spooled for subsequent weaving. All tows were then woven into high-quality, 8-harness satin fabrics. This particular fabric construction was chosen because it can be woven into a high-density product, uses less yarn than other weaves, it is highly pliable and readily conforms to compound curvatures and produces composites with high strength properties.

Comparative properties of the woven carbon fabrics are given in Table 5. The fabric breaking strengths are shown to be a strong function of the yarn carbonization temperatures. The highest-temperature-processed yarn $(1,350^{\circ}\text{C})$ yielded the strongest fabric.

TABLE 3

METHODS OF MANUFACTURING CARBON FABRICS

| METHOD | ATTRIBUTES | LIMITATIONS |
|--|---|--|
| PROCESSED FABRIC WEAVE OXIDIZED YARN/TOW PYROLYZE FABRIC | • EASIER TO WEAVE • ECONOMICAL | REQUIRES FILL YARN RESTRAINING MANUFACTURING DEVELOPMENT REQUIRED |
| • WOVEN FABRIC • PYROLYZE YARN/TOW • APPLY SURFACE FINISH • WEAVE CONSTRUCTION | HIGH STRENGTH & HIGH MODULUS UNIFORM PRODUCT MINIMUM INVENTORIES TAILORABLE CONSTRUCTIONS | • SLIGHTLY HIGHER COSTS |

TABLE 4
PROPERTIES OF DEVELOPMENTAL PAN-BASED CARBON FABRICS

| TYPE | 8-H FABRIC | 8-H FABRIC | 8-HS FABRIC |
|------------------------|-----------------------|-------------------------------------|----------------------|
| PROCESS | WOVEN OXIDIZED PAN | CARBONIZED WOVEN OXIDIZED PAN | WOVEN CARBON YARN |
| FIBER PROPERTIES | | | |
| DENSITY, Gm/cc | 1.30 | 1.78 | 1.72 |
| DIAMETER, Microns | 10.3 | 7.5 | 7.5 |
| TENSILE STRENGTH, Kpsi | | | |
| WARP | 24 | 261 | 336 |
| FILL | 56 | 315 | 363 |
| TENSILE MODULUS, Mpsi | | | |
| WARP | 1.1 | 25.7 | 30.8 |
| FILL | 1.2 | 29.5 | 30.7 |
| FABRIC PROPERTIES | | | |
| WEIGHT, oz/sq/yd | 13.2 | 8.2 | 11.8 |
| THICKNESS, In | 0.028 | 0.024 | 0.028 |
| THREAD COUNT, YARNS/In | | | |
| WARP | 16 | 18 | 25 |
| FILL | 91 | 18 | 52 |
| BREAK STRENGTH, 1b/In | | | |
| WARP | 134 | 193 | 364 |
| FILL | 147 | 144 | 385 |
| | | | |

TABLE 5

PROPERTIES OF COMMERCIAL AND DEVELOPMENTAL 8-HS WOVEN CARBON FABRICS

| PRECURSOR | * RAYON | * PAN | PAN | PAN | PAN | PAN |
|-----------------------|---------|---------|---------|---------|--------|-------|
| MAX. PROCESS TEMP. | 1,200°C | 1,350⁰C | 1,125°C | 1,075°C | 1,000℃ | ე₀006 |
| FIBER PROPERTIES | | | | | | |
| DENSITY, gm/cc | 1.53 | 1.77 | 1.81 | 1.81 | 1.82 | 1.75 |
| CARBON CONTENT, % | 95.5 | 96.2 | 86.9 | 86.4 | 81.8 | 81.1 |
| MOISTURE CONTENT, % | 6.0 | 0.4 | 1.2 | 3.4 | 6.2 | 6.3 |
| 푑 | 1 | 7.2 | 6.7 | 6.9 | 7.0 | 6.9 |
| FABRIC PROPERTIES | | | | | | |
| WEIGHT, 02/sq yd | 8.2 | 11.0 | 9.7 | 10.8 | 12.8 | 11.6 |
| THICKNESS, in | 0.018 | 0.027 | 0.023 | 0.028 | 0.024 | 0.032 |
| THREAD COUNT, ends/in | | | | | | |
| WARP | 53 | 24 | 20 | 24 | 24 | 20 |
| FILL | 20 | 23 | 20 | 24 | 24 | 20 |
| BREAK STRENGTH, Ib/in | | | | | | |
| WARP | 42 | 850 | 009 | 495 | 482 | 464 |
| FILL | 29 | 843 | 637 | 267 | 594 | 547 |

* COMMERICALLY AVAILABLE

Certain ablative applications require the use of very pure carbon fabrics. Less then several hundred parts per million of alkali metals are required because these metals can be ionized at high temperatures and greatly increase the electron concentration in ablation products-air boundary layer surrounding a reentry body (Reference 77).

The developmental PAN-based carbon fabrics had alkali metal contents of only 294 to 366 parts per million or less. Such products were obtained by using high-purity, foreign-source PAN fibers and clean weaving conditions. (See Table 6.)

Woven carbon fabrics are relatively low-cost products. Standard rayon-based and PAN-based carbon fabrics are on the order of \$50.00 per pound, see Figure 4. Special carbon fabrics woven from developmental carbon tows ranged in costs from \$150.00 to \$200.00 per pound. With increased usage, however, the costs of these specialty fabrics would be significantly reduced.

TABLE 6
CHEMICAL COMPOSITION OF DEVELOPMENTAL PAN-BASED CARBON FABRICS

| MAX. PROCESSING TEMP, ^O C | 1,350°C | 1,125°C | າ,075 ⁰ ເ | າ,000,ເ | ე ₀ 006 |
|--|---------|---------|----------------------|---------|--------------------|
| COMPOSITION Wt. | | | | | |
| CARBON | 96.2 | 6.98 | 86.4 | 81.8 | 0.18 |
| NITROGEN | 3.2 | 8.9 | 10.8 | 14.6 | 16.2 |
| HYDROGEN AND A COMPANY AND A C | 0.1 | 0.3 | 0.2 | 0.4 | 0.1 |
| NA CE | 0.3 | 3.0 | 2.0 | 3.2 | 1.5 |
| 0112 1110 | ì | ĭ | • | i | 0.) |
| ASH | 0.3 | 0.2 | 0.3 | 0.1 | 0.2 |
| | | | | | |
| ALKALI METALS, ppm | | | | | |
| William | 16 | 69 | 85 | 29 | 09 |
| MILLOSATOR | 32 | 16 | 23 | 18 | 20 |
| MITOLOGY | 378 | 233 | 179 | 200 | 170 |
| CALCION MACNES INM | 78 | 48 | 65 | 61 | 44 |
| mateness for TOTAL | 479 | 366 | 352 | 341 | 294 |

APPROXIMATE COSTS OF COMMERCIAL AND PURIFIED RAYON-BASED AND PAN-BASED CARBON FABRICS FIGURE 4.

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SECTION VII

PHENOLIC PREPREG

Standard phenolic resin impregnation techniques were used to obtain prepregged fabrics. Compared to rayon-based carbon fabrics, the newly available PAN precursor carbon fabrics exhibited lower resin wettability and slightly lower resin contents. Suitable prepregs were obtained, however, with resin contents on the order of 32 to 36 weight percent, five to seven-percent volatiles and four to six-percent flow.

SECTION VIII

FLAT LAMINATE COMPOSITES

A number of two-inch-thick composites were fabricated to gain experience with the developmental phenolic prepregs. Carbon fabrics manufactured at the upper and lower pyrolysis temperatures of interest were used, with particular emphasis on the mechanical adequacy of the 900°C processed material. Various molding temperatures and pressures were used to identify fabrication conditions yielding a predetermined resin content in the laminate. All composites were fabricated using a molding-to-stop method.

High quality laminates were obtained using standard fabrication conditions. Properties generated on the laminates indicated that a carbon fabric processing temperature of about $1,000^{0}$ to $1,075^{0}$ C would yield the best balance of low thermal conductivity, high strength and high carbon content.

SECTION IX

CYLINDRICAL COMPOSITES

The tapewrapping process is widely used to obtain cylindrical and frusta configurations (References 78 to 80). Hollow cylinders were therefore fabricated to gain experience with the developmental prepregs, obtain baseline composite properties, and to identify candidate materials for follow-on evaluation efforts. The developmental, non-surface treated carbon fabrics were prepregged with an unfilled phenolic resin, cut into tapes at 450 to the warp direction, sewn together into continuous strips, and slit into the desired tape width as illustrated in Figure 5. The tape was then wrapped onto a hollow cylindrical part using standard fabrication procedures, which is illustrated in Figure 6. The tape was hand-fed onto a cylindrical metal mandrel with the rough (fill) side against the mandrel. The wrap was anchored by lag-wrapping glass adhesive tape just after the application of the bias tape. The force of the pressure roller was approximately 200 lb/in of tape width. The wrapped composite was debulked in an autoclave to achieve a higher composite density. Typical debulking conditions were 300 psi at 1750F for one hour. The cylinders were then machined to a predetermined outside diameter that was adequate to fit into the female cure fixture. After machining, the cylinders were removed from their mandrel and loaded into the cure fixture together, with a bleeder cloth and a rubber bag. Vacuum was applied and the assembly placed into a hydroclave. The part was then cured initially at 180°F and incrementally pressurized to 1,000 psi with the temperature rising to about 3100 and maintained for four hours. The cylindrical specimens were nine inches in length, nine inches in outside dimension and one-half inch in thickness. The fabric angle was 200 to the axial direction.

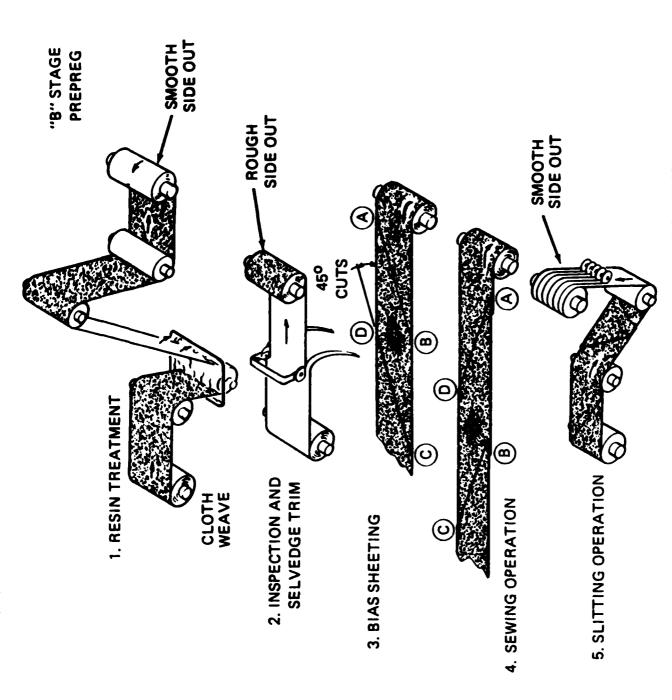


FIGURE 5. METHOD OF PREPARING PHENOLIC CARBON TAPE PREPREG

FIGURE 6. ILLUSTRATION OF THE TAPE WRAPPING PROCESS

SECTION X

COMPOSITE PROPERTIES

1. GENERAL:

Ablative, thermophysical, chemical and mechanical properties of the 20° tapewrapped carbon fabric/phenolic composites were measured at room and high temperatures. These engineering properties were compared to values obtained for baseline rayon-based carbon fabric/phenolic composites to permit the identification of attributes, limitations and improvement needs.

2. ABLATION:

Extensive investigations have been conducted on the ablative characteristics of carbon fabric/phenolics in ground-based test facilities and reentry vehicle flight tests (References 26 to 28, 79 to 82). Materials properties and characteristics of interest include: linear and mass ablation rates, quality of the surface Jegraded char layer, and surface ablation patterns.

The recession characteristics of various PAN-based carbon fabric/phenolic composites were determined in high-temperature, arc-heated air. Flat plate specimens were immersed in turbulent, supersonic flow environments using the Avco Corporation 10MW Air Arc Facility, as illustrated in Figure 7. Typical test conditions included an air enthalpy of 7,300 to 7,400 Btu/lb, cold-wall heating flux of 1,000 to 1,100 Btu/ft²-sec, shear stress of 45 lbs/sq ft and a test time of 15 seconds (References 83 and 84).

FIGURE 7. SCHEMATIC OF THE 2D ABLATION WEDGE TEST ARRANGEMENT

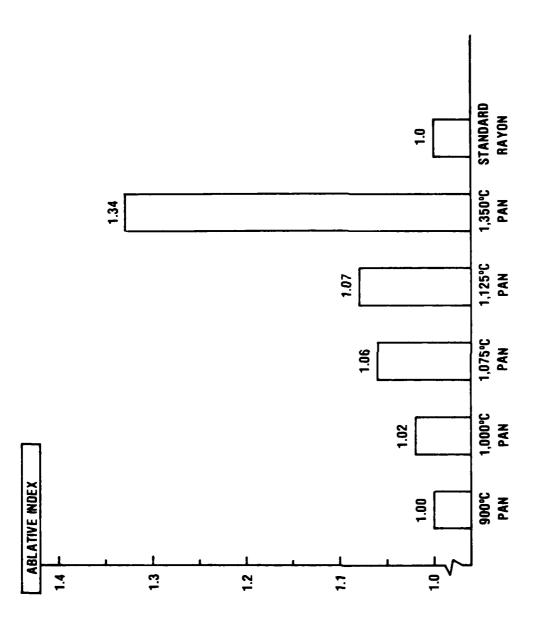
Ablated composite specimens were cross-sectioned to examine their indepth appearance. (See Figure 8.) Each material contained an outer porous layer, an underlying thermally degraded region and the substrate intact region. The ablated rayon-based carbon fabric/phenolic specimen was more porous in the surface region and the carbon fabric plies were distorted from their original 20° orientation. The ablated PAN-based carbon fabric/phenolic had a densier charred surface layer and the porosity was more uniform in distribution and pore size. The more dense char layer suggests higher resistance to shear and erosion stresses, although experimental tests have not been run todate to confirm the hypothesis.

The normalized rates of ablation for various available carbon fabric/phenolic composites are given in Figure 9. The high temperature fired PAN-based carbon fabric/phenolic exhibited a significantly higher ablation rate, i.e., about 34%. Lower-temperature-fired PAN-based carbon fabric/phenolic composites, however, exhibited ablation rates comparable to state-of-the-art rayon-based carbon/phenolics. To summarize, the developmental PAN-based carbon fabric/phenolics had about equivalent linear ablation rates as compared to baseline materials.





CROSS-SECTIONAL PHOTOGRAPHS OF ABLATED RAYON-BASED (LEFT) AND PAN-BASED (RIGHT) CARBON FABRIC/PHENOLIC COMPOSITES FIGURE 8.



RELATIVE LINEAR ABLATION RATE OF COMMERCIALLY AVAILABLE AND DEVELOPMENT CARBON FABRIC/PHENOLICS FIGURE 9.

3. THERMOPHYSICAL PROPERTIES:

<u>Density</u>. Composites containing PAN-based carbon fabrics were slightly higher in density as compared to baseline rayon-base carbon/phenolics. As shown in Table 7, the new PAN-based carbon/phenolics had densities about ten percent higher than state-of-the-art composites.

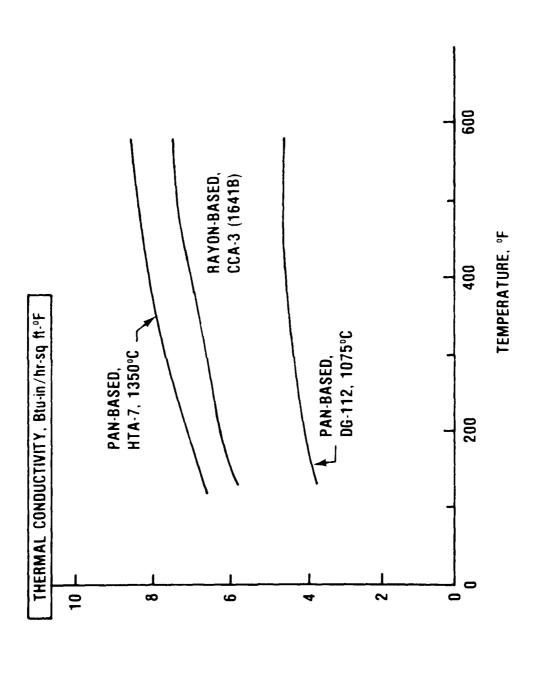
Thermal Conductivity. PAN-based carbon fabrics woven from high temperature fired yarns and tows are quite crystalline and hence thermally conductive (References 72, 73, 85). Tapewrapped phenolic composites containing these reinforcements are thus more thermally conductive than baseline rayon-based carbon/phenolics as shown in Table 7. Composites containing developmental, lower temperature fired carbon fabrics exhibit significantly lower composite conductivities. For example, the 1,075°C processed PAN-based carbon fabric/phenolic exhibited about 34% lower thermal conductivity as compared to the baseline rayon-based carbon/phenolic. The improved thermal conduction features of the developmental PAN-based carbon/phenolics were maintained at higher temperatures, as illustrated in Figure 10. It is thus apparent that significant weight savings can be realized by the use of highly insulative, PAN-based carbon fabric composites.

Thermal Expansion. Resinous composites typically have high thermal expansion coefficients because of the matrix. Carbon fabrics significantly restrain the expansion and contraction of matrices, depending upon the fiber properties and the direction of reinforcement. Phenolic composites reinforced with low modulus, rayon-based carbon fabrics exhibit significant expansion with temperature as shown in Figure 11. The more thermally stable PAN-based carbon fabric reinforced composites exhibited little change with temperature, but the lower temperature processed carbon fabric/phenolics underwent some shrinkage with temperature.

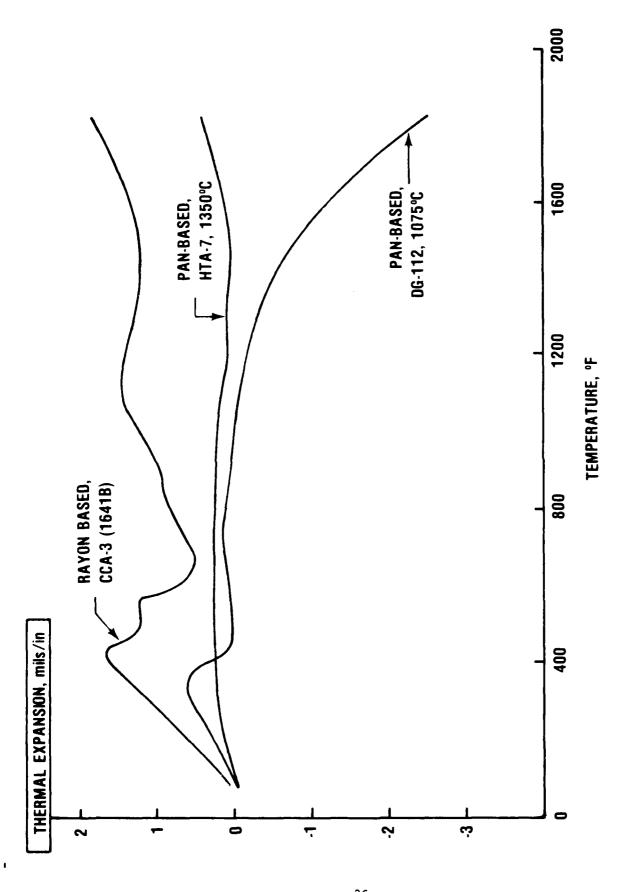
TABLE 7

THERMOPHYSICAL PROPERTIES OF 200 TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES

| MATERIAL DESCRIPTION | PAN-BASED, | PAN-BASED, | RAYON-BASED, |
|-------------------------|----------------|-----------------|---------------|
| FABRIC | HTA-7 (1350°C) | DG-112 (1075°C) | CCA-3 (1641B) |
| PHENOLIC, Wt. % | 31.4 | 36.8 | 38.0 |
| COMPOSITE PROPERTIES | | | |
| DENSITY, gm/cc | 1.58 | 1.57 | 1.43 |
| POROSITY, Vol. % | 2.49 | 1.62 | 6.42 |
| SPECIFIC HEAT, 250°F | | | |
| Btu/lb-9F | 0.28 | 0.30 | 0.32 |
| THERMAL CONDUCTIVITY, | | | |
| RADIAL DIRECTION, 250°F | 7.2 | 4.3 | 6.5 |
| Btu-in/hr-sq ft.ºF | | | |
| THERMAL EXPANSION, | | | |
| 250°F, mils/in | | | |
| H00P | 0.2 | 0.4 | 8.0 |
| AXIAL | 0.4 | 1.0 | 1.0 |
| RADIAL | 2.0 | 2.0 | 2.0 |



THERMAL CONDUCTIVITIES OF 200 TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES AT ELEVATED TEMPERATURES FIGURE 10.



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HOOP THERMAL EXPANSION OF 200 TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES AT ELEVATED TEMPERATURES FIGURE 11.

4. CHEMICAL PROPERTIES:

Composite Compositions. As previously discussed, rayon-based carbon fabrics are typically purified to reduce their alkali metal concentrations. The resultant composites are thus very pure, with only minor contaminants added via the phenolic resin, carbon powder filler and fabrication conditions. PAN-based carbon fabrics are significantly more impure because no or few precautions have been taken to obtain very pure materials. Commercially available phenolic composites are about three times more contaminated than purified rayon-based carbon/phenolic composites, as shown in Table 8. It is apparent that special processing steps are required to synthesize pure PAN polymer, process it into non-contaminated fibers, develop chemical purification processes and carbonize into the desired fibers in the absence of unwanted impurities. Table 8 presents information on the relative impurities of rayon-base and PAN-based carbon fabric/phenolic composites.

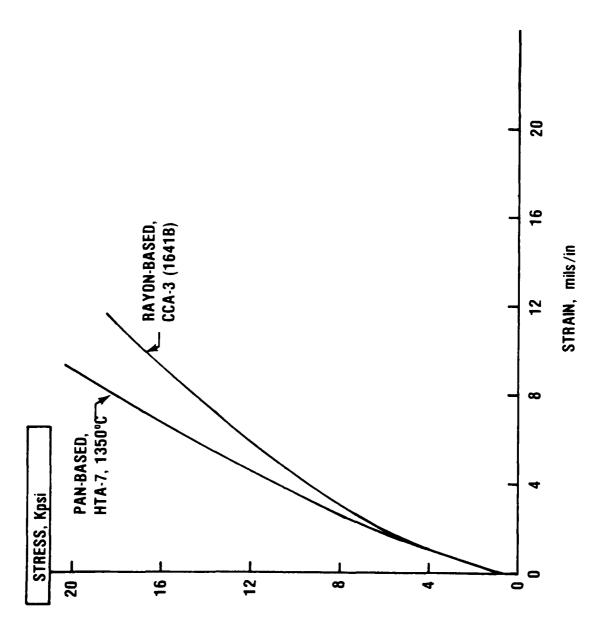
5. MECHANICAL PROPERTIES:

The excellent structural properties of PAN-based carbon fabrics are also realized in composites thereof. Maximum mechanical properties are obtained when the composite is stressed parallel to the direction of the reinforcement. At other angles of reinforcement, composite mechanical properties are greatly reduced.

The hoop tensile stress-strain relationships for two 20⁰ tapewrapped phenolic composites are shown in Figure 12. The PAN-based carbon fabric/phenolic composite had a maximum strength and strain-at-failure comparable to commercially available rayon-based carbon fabric/Phenolic. At elevated

TABLE 8
CHEMICAL CONTAMINANTS IN CARBON FABRIC/PHENOLIC COMPOSITES

| | COMPOSITE DESCRIPTION | BASELINE CARBON/PHENOLIC | PAN-BASED CARBON/PHENOLIC |
|----|----------------------------|--|--------------------------------|
| | RESIN | PHENOLIC, 34 Wt. % | PHENOLIC, 32 Wt. 3 |
| | FILLER | CARBON POWDER, 10 Wt. % | NONE |
| | FABRIC | CCA-3 (1641B) RAYON-BASED, 56 Wt. % | 1,350°C PAN-BASED, 68 Wt. % |
| | CHEMICAL CONTAMINANTS, ppm | | |
| | SODIUM | 39 | 99 |
| 38 | POTASSIUM | ß | 15 |
| } | CALCIUM | 10 | 19 |
| | MAGNESIUM | 6 | 19 |
| | LITHIUM | - | |
| | TOTAL | 64 | 162 |



HOOP TENSILE STRESS:STRAIN RELATIONSHIPS FOR TWO TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES FIGURE 12.

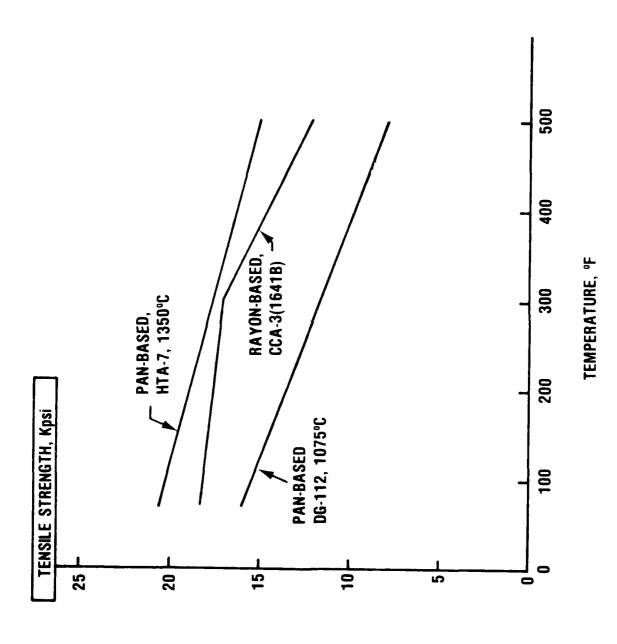
temperatures, the slightly higher tensile hoop strength of the PAN-based carbon fabric/phenolic was maintained over a range of 75° to 500°F. A linear decrease in tensile strength with temperature was obtained as noted in Figure 13. Also shown in Figure 13 is the superior tensile strengths obtained with the commercially available (1,350°C) PAN-based carbon fabric compared to the developmental 1,075°C carbon fabric. The cause of the reduced hoop strength was not investigated, but it should be noted that no effort was taken to clean or influence the fiber:matrix bond of the developmental carbon fabrics.

Table 9 presents additional mechanical properties of three tapewrapped carbon fabric/phenolic composites. Tensile and compressive properties in the hoop and axial directions are reported at room temperature conditions. Typical hoop mechanical properties for the optimized 1,075°C processed carbon fabric/phenolic included a tensile strength of 15,600 psi, a tensile modulus of 2.97 million psi, a tensile strain-to-failure of 11.5 mils per inch, a compressive strength of 18,200 psi, a compressive modulus of 2.17 million psi, and a compressive strain-to-failure of 33.5 mils per inch. Although these structural properties are lower than rayon-based carbon fabric analogues, they appear to be adequate for most ablative heat-shielding applications.

The lowest mechanical property of tapewrapped PAN-based carbon fabric/
phenolic composites was interlaminar shear strength, as shown in Figure 14.

At room temperature, the shear strengths of commercial and developmental

PAN-based carbon fabric/phenolics were about one-half the values for baseline rayon-based carbon fabric composites. The strength values were reduced
with increasing temperature, although the rayon-based carbon fabric composite



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HOOP TENSILE STRENGTHS OF THREE TAPEWRAPPED CARBON FABRIC/PHENOLICS AT ELEVATED TEMPERATURES FIGURE 13.

TABLE 9

MECHANICAL PROPERTIES OF 200 TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES

| MATERIAL DESCRIPTION | PAN-BASED, | PAN-BASED, | RAYON-BASED |
|--------------------------------------|----------------|-----------------|---------------|
| FABRIC | HTA-7 (1350°C) | DG-112 (1075°C) | CCA-3 (1641B) |
| PHENOLIC Wt. % | 31.4 | 36.8 | 38.0 |
| COMPOSITE PROPERTIES | | | |
| TENSILE STRENGTH, Kpsi | | | |
| H00P | 20.3 | 15.6 | 18.3 |
| AXIAL | 3.7 | 5.7 | 8.3 |
| TENSILE MODULUS, Mpsi | | | |
| HOOP | 3.50 | 2.97 | 2.82 |
| AXIAL | 1.40 | 1.90 | 2.05 |
| TENSILE STRAIN, mils/in | | | |
| H00P | 9.1 | 11.5 | 11.7 |
| AXIAL | 1.7 | 3.2 | 4.3 |
| COMPRESSIVE STRENGTH, Kpsi | _ | | |
| H00P | 18.7 | 18.2 | 33.5 |
| AXIAL | 13.0 | 13.4 | 31.7 |
| COMPRESSIVE MODULUS, Mpsi | | | |
| HOOP | 2.60 | 2.17 | 2.36 |
| AXIAL | 1.70 | 2.01 | 2.24 |
| INTERLAMINAR SHEAR STRENGTH, Kpsi | 2.78 | 3.30 | 6.57 |

INTERLAMINAR SHEAR STRENGTH OF THREE TAPEWRAPPED CARBON FABRIC/PHENOLIC COMPOSITES FIGURE 14.

was more affected by temperature. At 500°F, the shear strength of the PAN-based composite was about 1,600 psi whereas the rayon-based composite had a value of about 3,000 psi. These property values are adequate for nonstructural ablative applications, although higher interlaminar shear strengths would be desirable.

The interlaminar shear strength of composites is a strong function of fiber surface chemistry, microporosity and topography (References 86 and 87). There are apparently different amounts of acidic and alkaline surface oxides on the fibers which greatly influence fiber wettability and fiber: matrix bonding. For phenolic composites, the mechanical properties are closely related to the fiber surface carboxylic groups. Adhesion between fiber and phenolic matrix is realized primarily by chemical bonding, and to a much lesser degree, the surface roughness. Lastly, the increased surface microporosity noted for the developmental, lower temperature fired carbon fibers may indirectly influence composite shear strength. The developmental carbon fibers are more hydrophilic, which in turn affect fiber wetting, prepreg solvent retention, resin pickup, general handling characteristics and composite shear properties.

SECTION XI

CONCLUSIONS

1. PRECURSOR FIBERS:

Carbonaceous fibers are specialty engineering materials which are used in a variety of defense, aerospace, industrial, and scientific applications.

Continuous filament rayon is the most commonly used precursor for fibrous carbon products.

There is presently a single qualified manufacturing source for aerospace grade, continuous filament rayon yarn.

Polyacrylonitrile is a leading alternate precursor for fibrous carbons.

Continuous processes have been developed for manufacturing PAN-based carbon yarns and tows.

The use of PAN in lieu of rayon results in higher carbon yields and shorter processing times.

PAN-based carbon and graphite fibers have been researched extensively since 1961 by organizations in Japan and Great Britain. In contrast, manufacturers in the United States have focused on rayon precursors until recent years.

Polyacrylonitrile fibers have high carbon contents and are available in various filament count yarns and tows. Costs are moderate, the commercial market is stable, and the fibers are available from many sources throughout the industrialized world.

Composition of matter and manufacturing methods for PAN-based carbon and graphite fibrous products are described in hundreds of world patents and published articles.

Continuous filament PAN used in the manufacture of carbon fabrics is produced by foreign sources. A domestic source is desired for small-filament-count PAN yarns or tows.

Manufacturing temperatures used in the production of carbon and graphite fibers have been optimized to obtain the best balance of fiber yield, strength and modulus. Lower processing temperatures result in lower density, higher porosity, and lower thermal conductivity fibrous products.

Only a small fraction of PAN fiber production is required for defense needs. Moreover, the defense requirements are highly cyclic.

The surface microporosity of low-temperature-fired PAN fibers influences their hydroscopic nature and leads to reduced fiber wetting by phenolic matrices.

2. CARBON FIBERS AND FABRICS:

Carbon fabrics derived from PAN-based cloths typically have a high fiber density, moderate to high alkali metal content, and moderate-to-low thermal conductivity.

Thin fabrics woven from 1,000 to 3,000 filaments are close to optimum from the standpoint of composite fabrication, balanced properties and costs.

Oxidized yarns or tows are easy to weave into fabric, but the fabric quality is difficult to maintain during pyrolysis because of the differential shrinkage of warp and fill reinforcements.

High quality, PAN-based carbon fabrics were woven into 8-harness satin construction with conventional machinery.

A lubricant is required to weave carbon fabrics, although the fibers have considerable abration resistance.

Very high strength carbon fabrics are produced by weaving high strength carbon yarns.

Carbon fabrics represent the largest usage of fibrous carbons. They have been produced in plain, 5-harness, and 8-harness woven fabrics.

Carbon fabrics derived from 1,057°C processed yarn yielded the best balance of properties for thermal shielding applications.

Developmental PAN-based carbon fabrics had alkali metal contents from 294 to 366 parts per million. An order of magnitude reduction in contaminants is needed to enhance their potential for heatshielding uses.

Developmental PAN-based carbon fabrics are about two to three times the cost of commercial grade materials. Costs will decrease in direct proportion to increased volume requirements.

Commercially available, PAN-based carbon cloths are suitable for use in many thermal protection composites.

Commercially available, PAN-based carbon fabrics are not presently suitable for missile heatshielding because of their alkali metal contaminant levels.

Commercially available, PAN-based carbon fabrics possess very high strength properties, which lend themselves to advanced aircraft structural composite uses.

3. FABRICATION:

State-of-the-art fabrication methods were modified slightly to obtain thick plastic laminates with the developmental phenolic prepregs.

High quality, tapewrapped cylinders were fabricated with commercially available and developmental PAN-based carbon fabrics.

4. COMPOSITE PROPERTIES:

Speciality PAN-based carbon fabrics and phenolic composites thereof were manufactured with insulative characteristics superior to baseline rayon-based material.

Excellent structural properties of PAN-based carbon fabrics are not realized in tapewrapped phenolic composites because the stress direction is typically at a large angle to the fabric orientation.

Rayon-based carbon fabric/phenolic composites were found to have better high temperature structural properties compared to the PAN-based carbon fabric reinforced composites, except in the plane of the woven fabric.

The speciality PAN-based carbon fabrics exhibited lower thermal expansion compared to rayon-based material.

PAN-based carbon fabric/phenolic composites formed a desired dense surface layer during ablation.

The linear ablation rate of commercially available PAN-based carbon fabric/phenolics was about 34% higher than state-of-the-art rayon-based carbon fabric/phenolics.

Low temperature fired (developmental) PAN-based carbon fabric/phenolics had about the same linear ablation rates compared to rayon-based carbon fabric/phenolic composites.

Carbon/phenolic composites composed of commercially available PAN-based carbon fabrics had higher thermal conductivities than rayon-based carbon fabric/phenolics.

PAN-based carbon fabric/phenolic composites exhibited low thermal expansion features.

Phenolic composites containing developmental PAN-based carbon fabrics had about two-thirds the thermal conductivity of baseline rayon-based carbon fabric/phenolics.

Commercially available PAN-based carbon fabric/phenolics contained about three times the level of alkali metal contaminants desired for missile heatshielding applications.

The mechanical properties of PAN-based carbon fabric/phenolics were adequate for heatshielding applications.

The interlaminar shear strength was the lowest mechanical property of the carbon fabric/phenolics. Developmental carbon fabrics possessed low composite shear strengths because no effort has been made to stabilize the fiber surface.

The composite interlaminar shear strength of PAN-based carbon reinforcements was relatively low primarily because no effort has been expended to clean or stabilize the fiber surfaces.

The relatively low interlaminar shear strength of the PAN-based carbon fabric/phenolic composites is believed to be due to poor fiber-matrix bonding, and, large differences in expansion characteristics between the phenolic matrix and the fabric.

SECTION XII

RECOMMENDATIONS

Future PAN-based carbon fabric developmental efforts should address high chemical purity, economic weaving, fiber surface treatments and domestic availability issues.

Very pure PAN-based carbon fibers should be investigated by developing chemical purification processes, or using ultra-pure polyacrylonitrile and clean fiber formation methods.

Full width (33 to 36 inches) carbon fabrics should be made available to maximize the length of bias slit tape.

The detailed carbon fiber surface properties and characteristics should be measured to provide insights on improving the fiber-to-phenolic bond strength. Properties of particular importance include: surface area, polarity, energy, heterogeneity, microstructure and chemical composition.

Surface treatments should be developed to stabilize PAN-based carbon fiber surfaces, enhance phenolic resin wettability, and promote increased interlaminar shear strength in the composite.

Domestic sources should be developed for aerospace grade, continuous, samll filament count (1,000 to 3,000) polyacrylonitrile fibers.

APPENDIX A

GLOSSARY OF TERMINOLOGY

Ablation: Physical removal and thermal degradation of a material due to incident thermal/mechanical/chemical environmental parameters.

Acrylonitrile: A monomer with the structure (CH2:CHCN).

Anisotropic: Different values of a property in different directions. Non-isotropic.

Ash Content: The solid residue remaining after a reinforcing substance has been incinerated (or strongly heated).

<u>Autoclave</u>: A closed vessel for conducting a chemical reaction or other operation under pressure and heat.

<u>Autoclave Molding</u>: A process similar to the pressure bag technique. The layup is covered by a pressure bag, and the entire assembly is placed in an autoclave capable of providing heat and pressure for curing the part. The pressure bag is normally vented to the outside.

<u>B-Stage</u>: An intermediate stage in the reaction of a thermosetting resin in which the material is partially advanced in its cure to a point to facilitate handling and processing.

<u>Binder</u>: A fluid materials like a resin, used to contain fibrous reinforcements in composites.

<u>Bonding</u>: Jointing together of two dissimilar materials, like a fibrous reinforcement and a matrix.

<u>Carbon Fiber</u>: Fiber formed by the controlled pyrolysis of precursory organic fiber such as viscose rayon, polyacrylonitrile, phenolic, pitch, etc.

<u>Carbonization</u>: Thermal process by which high carbon-containing substances are formed, and the resultant material has an amorphous or turbostratic structure.

Characteristic: A distinguishable feature of a material, which is partially dictated by the environmental parameters.

<u>Coefficient of Thermal Expansion</u>: The change in volume per unit volume produced by a one-degree rise in temperature.

<u>Composite</u>: A material consisting of two or more discrete physical phases, in which a fibrous phase is dispersed within a continuous matrix phase.

<u>Compression Molding</u>: Process for producing essentially parallel to the surface orientation of reinforcement in composites.

<u>Compressive Strength</u>: The maximum compressive load sustained by a specimen during a compression test, divided by the original cross-sectional area.

<u>Condensation Polymer</u>: A polymer from one or more types of monomers, with the elimination of water or some other simple substance. Phenolic resins are of this type.

<u>Contaminant</u>: An impurity or foreign substance present in a material which affects one or more properties of the material.

<u>Continuous Filament Yarn</u>: Yarn formed by twisting two or more continuous filaments into a single, continuous strand.

<u>Copolymer</u>: A molecule formed when two or more dissimilar monomers add to the growing polymeric chain.

<u>Count</u>: The number of warp yarns (ends) and filling yarns (picks) per inch in woven cloth; for example, 30 X 40 or 30 ends of warp X 40 picks of filling.

Crack: Visible delamination or material separation.

Crosslinked: A three dimensional network of a polymeric material.

 $\overline{\text{Cure}}$: To change the properties of a resin by chemical reaction, which may be condensation or addition; usually accomplished by the action of either heat or catalyst, or both, and with or without pressure.

<u>Debulking</u>: Compacting of thick laminates under moderate heat and vacuum to insure seating on the tool and to prevent wrinkles.

<u>Decomposition</u>: A chemical and physical breakdown due to excess exposure to heat.

<u>Deformation</u>: Change in shape or dimension of a material accompanying a stressed condition or associated with the application of a stress.

Delamination: The separation of the layers of material in a laminate.

<u>Denier</u>: A unit of weight expressing the size or coarseness of a fiber or yarn. The weight in grams of 9,000 meters of a fiber or yarn.

<u>Elastic Modulus</u>: Ratio of the stress or load applied to the strain or deformation produced in a material that is elastically deformed.

Elongation: Fractional increase in length of a material stressed in tension.

End: An individual warp yarn, thread, monofilament or roving.

<u>Fabric</u>: Fabrics are usually described according to the type of weave and the number of yarns per inch, first in the warp direction (parallel to the length of the fabric), then in the fill direction (perpendicular to the warp). For example, a 30 X 28 fabric has 30 yarns/in. in the warp direction and 28 yarns/in. in the fill direction.

<u>Fiber</u>: An elongated form of a material that has a minimum length to a maximum average transverse dimension of ten-to-one and a maximum cross-sectional area of 0.000079 square inch.

<u>Fiber Content</u>: The amount of fiber present in a composite. This is usually expressed as a percentage volume fraction or weight fraction of the composite.

<u>Fiber Direction</u>: The orientation or alignment of the longitudinal axis of the fiber with respect to a stated reference axis.

Fiber Volume: The volume of fiber in a cured composite. Typical for carbon fiber/phenolic composites is 50 to 70 volume %.

Filament: The basic structural fibrous element. It is continuous or very long compared to its average diameter, which is usually 6 to 10 microns.

Fill: Yarn oriented at right angles to the warp in a woven fabric (also called weft).

<u>Filler</u>: A solid material used in carbon and graphite articles, usually in particulate or short fiber forms.

<u>Flexural Modulus</u>: The ratio, within the elastic limit, of the applied stress on a test specimen in flexure to the corresponding strain in the outermost fibers of the specimen.

Flexural Strength: The resistance of a material to being broken by bending stresses.

Flow: The movement of resin under pressure, allowing it to fill all parts of a mold; flow or creep - the gradual but continuous distortion of a material under continued load, usually at high temperatures.

<u>Fracture</u>: The separation of a body.

High Pressure Laminating: A matched-die technique used to form thick laminates.

<u>Hoop Stress</u>: The circumferential stress in a material of cylindrical form subjected to internal or external pressure.

<u>Hydroscopic</u>: The property denoted by absorbing and retaining an appreciable quantity of moisture from the air.

Impregnate: In reinforced plastics, the saturation of the reinforcement with a resin.

Impregnated Fabric: A fabric impregnated with a synthetic resin (see "Prepreg.")

<u>Interface</u>: The boundary between the individual, physical distinguishable constituents of a composite.

Interlaminar: Descriptive term pertaining to some object (e.g., voids), event (e.g., fracture), or potential field (e.g., shear stress) referenced as existing or occurring between two or more adjacent laminae, between the plies.

Interlaminar Shear: Shearing force tending to produce a relative displacement between two laminae in a laminate along the plane of their interface.

Isotropic: Identical properties in all directions.

<u>laminate</u>: A product made by bonding together two or more layers or laminae of material or materials.

<u>Layup</u>: A process of fabrication involving the placement of successive layers of materials.

<u>Linear Expansion Coefficient</u>: The change in length per unit length resulting from a one degree rise in temperature.

Mandrel: A form fixture of male mold used for the base in the production of a part by layup or filament winding.

Matched-Die Molding: An automated, high production process in which resin is added to a pre-cut, shaped sheet of mat or fabric or to a preform heated match-die mold.

<u>Matrix</u>: The essentially homogeneous material in which the fibers or filaments of a composite are imbedded.

Molding: The forming of a polymer or composite into a solid mass of prescribed shape and size by the application of pressure and heat.

Modulus: The stress in pounds per square inch (of original cross section) required to produce a certain elongation or deformation.

Moisture Absorption: The pick-up of water vapor from air by a material.

<u>Molding</u>: The shaping of a material within or on a mold, which is normally accomplished with heat and pressure.

Off-Axis: At some angle to the major plane of reinforcement.

<u>Pattern-Layup</u>: Process for hand orientation of filaments or fabric into a predetermined surface orientation.

<u>Permeability</u>: The passage or diffusion of a fluid or solid through a barrier without physically or chemically affecting it.

pH: The measure of the acidity or alkalinity of a substance.

<u>Phenolic Resins</u>: A synthetic resin produced by the condensation of an aromatic alcohol with an aldehyde, particularly of phenol and formaldehyde.

<u>Plain Weave</u>: The simpliest of the fundamental weaves. Each filling yarn passes alternately under and over each warp.

<u>Plastic</u>: A high molecular weight substance including either natural or synthetic materials.

<u>Plied Yarn</u>: A yarn formed by twisting together two or more single yarns in one operation.

<u>Polymer</u>: A high molecular weight organic compound, whose structure can be representated by a repeating small unit.

<u>Polymerize</u>: To unite molecules of the same kind to form a compound having the <u>elements</u> in the same proportion but possessing much higher molecular weight and different physical properties.

<u>Porosity</u>: A condition of trapped pockets of air, gas, or void within a solid material, usually expressed as a percentage of the total nonsolid volume to the total volume (solid + nonsolid) of a unit quantity of material.

<u>Precursor</u>: A starting material which is changed chemically and physically to yield a new material having greatly different properties.

<u>Preform</u>: A preshaped fibrous reinforcement prior to the application of a matrix in forming a composite material.

<u>Prepreg</u>: Ready to process material in which the reinforcement has been impregnated with a resin and stored for subsequent use.

Pressure: Force measured per unit area.

<u>Post-Cure</u>: Application of heat after an initial cure, to further polymerize the material.

Property: A distinguishable feature of a material.

<u>Proportional Limit</u>: The point on the stress:strain curve at which stress ceases to be proportional to strain.

<u>Pyrolysis</u>: A constructive process involving relatively high temperatures to convert an organic material into a carbonaceous residue. The process of decomposing a material by heat.

Random: No fixed pattern.

Reinforcement: A strong inert material used to improve the mechanical properties of matrix materials.

Residue: The solid material remaining during pyrolysis of an organic.

Resin: A polymeric substance capable of being converted into a hard and rigid material through chemical or thermal means.

Resin Content: The amount of matrix present in a composite, either by percent weight or percent volume.

Roving: Composed of continuous filament and spun strand forms. Made by gathering a number of continuous filament strands, and winding them.

Satin Weave: In this construction, one warp end is woven over several successive fill yarns, then under one fill yarn.

<u>Shear</u>: An action or stress resulting from applied forces which causes or tends to cause two contiguous parts of a body to slide relative to each other in a direction parallel to their plane of contact.

<u>Shrinkage</u>: The relative decrease in dimension between the length measured before and after the application of a causative agent.

Solvent: A dissolving liquid to thin a resin.

Specific Gravity: The ratio of the weight of any volume of a substance to the weight of an equal volume of another substance taken as standard at a constant or stated temperature. Solids and liquids are usually compared with water at 4° C.

<u>Specific Heat</u>. The quantity of heat required to raise the temperature of a unit mass of a substance one degree under specified conditions.

<u>Splice</u>: The joining of two ends of fiber yarn or strand, usually by means of a glue or sewn threads.

Stiffness: The capacity of a material to resist elastic displacement under stress.

Strain: The ratio of the extension to the original length of the measured elongating section of the test specimen.

<u>Strand</u>: A primary bundle of continuous filaments combined into a single compact unit without twist.

Stress: The internal force per unit area which resists a change in size or shape of a body.

<u>Stress-Strain</u>: Stiffness, expressed in pounds per square inch or kilograms per square centimeter, at a given strain.

Stress-Strain Curve: Simultaneous readings of load and deformation, converted to stress and strain, are plotted as ordinates and abscissae, respectively, to obtain a stress-strain diagram.

<u>Substrate</u>: The region of a composite which is below the original surface.

Tack: Stickiness of a prepreg.

Tape: A narrow-woven fabric or narrow piece slit from broad goods.

<u>Tape-Wrap</u>: Process involving the application of a matrix impregnated woven fibrous tape to a rotating mandrel.

Tensile Modulus: Ratio of the tension stress to the strain in material.

<u>Tensile Strength</u>: The maximum tensile load per unit area of original cross-section, within the gauge boundaries of the specimen.

<u>Thermal Expansion Coefficient</u>: The change in volume per unit volume produced by a one degree rise in temperature.

<u>Toughness</u>: The energy required to break a material. This energy is equal to the area under the stress:strain curve.

<u>Tow</u>: A large bundle of continuous filaments, generally 10,000 or more, not twisted.

<u>Transverse</u>: Perpendicular or normal to the principal axis of reinforcement.

<u>Twist</u>: The turns about the axis of fibrous, yarns or cords.

Two-Directional Reinforcement: Fibrous reinforcement providing structural properties in two directions. Like a fabric reinforced composite. Also 2-D.

Unidirectional: Exhibiting major properties in one direction only.

<u>Vacuum Bag Molding</u>: A hand lay-up process in which the material is cured under pressure generated by drawing a vacuum in the space between the lay-up and a flexible sheet placed over it and sealed at the edges.

<u>Volatile Content</u>: The percent of volatiles which are driven of as a vapor from a plastic or an impregnated reinforcement.

Virgin: The original or intact state.

Warp: The longitudinally oriented yarn in a woven fabric; a group of yarns in long lengths and approximately parallel.

Weave: The particular manner in which a fabric is formed by interlacing yarns.

<u>Wettability</u>: Extent to which a resin completely surrounds and adheres to a reinforcement.

Yarn: A small, continuous bundle of filaments, generally fewer than 10,000. The filaments are lightly stranded together so they can be handled as a single unit. The yarn may be twisted to enhance bundle integrity.

Young's Modulus: The ratio of tensile stress to tensile strain below the proportional limit.

APPENDIX B

CONVERSION FACTORS FOR U.S. CUSTOMARY TO METRIC (S1) UNITS OF MEASUREMENT.

| To convert from | То | Multiply by |
|------------------------|--|--------------|
| mils | millimeters | 0.0254 |
| inches | centimeters | 2.54 |
| feet | meters | 0.3048 |
| miles | kilometers | 1,6093 |
| square inches | square centimeters | 6.4516 |
| square feet | square meters | 0.0929 |
| square miles | square meters | 2,589,998.0 |
| cubic inches | cubic centimeters | 16.38706 |
| cubic feet | cubic meters | 0.0283 |
| cubic yards | cubic meters | 0.764555 |
| gallons (U.S.) | liters | 3.785 |
| gallons (Imperial) | liters | 4.542 |
| ounces | grams | 28.349 |
| pounds | kilograms | ().454 |
| tons (short) | kilograms | 907.185 |
| tons (long) | kilograms | 1,016.047 |
| pounds per foot | newtons per meter | 14.59390 |
| pounds per square inch | newtons per square centimeter | 0.6894757 |
| pounds per cubic inch | kilograms per cúbic centimeter | 27,679.90 |
| pounds per square foot | newtons per square meter | 47.88026 |
| pounds per cubic foot | kilograms per cubic meter | ره 10. 16 |
| inches per second | centimeters per second | 2.54 |
| inch-pounds | meter-newtons | 0.1129848 |
| inch-kips | meter-kilonewtons | 0.0001129848 |
| Fahrenheit degrees | Celsius degrees or Kelvins ^a | 5/9 |
| kilotons | terajoules | 4.183 |

^aTo obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use C = (5/9) (F - 32). To obtain Kelvin (K) readings, use K = (5/9) (F - 32) - 273.15.

APPENDIX C

| SYMBOLS | DEFINITIONS |
|-----------------|---------------------------------|
| Btu | British Thermal Unit |
| cal | calculated or calories |
| cc | cubic centimeter |
| cm | centimeter |
| co ₂ | carbon dioxide |
| est | estimated |
| ft | foot |
| gm | gram |
| hr | hour |
| нѕ | harness satin weave |
| in | inch |
| k | thermal conductivity |
| Kpsi | 1,000 psi |
| 16 | pound |
| m | meter |
| micro | one millionth |
| mils | one thousandth of an inch |
| min | minute |
| Mpsi | 1,000,000 psi |
| MW | megawatt |
| 0 Z | ounce |
| PAN or Pan | polyacrylonitrile |
| рΗ | degree of acidity or alkalinity |
| ppm | parts per million |
| psi | pounds per square inch |

APPENDIX C (CONT'D)

SYMBOLS DEFINITIONS second sec square sq temperature temp volume vol weight wt times X yd yard percent % οс degree Centrigrade ٥_F degree Fahrenheit micron dollars

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